Thermal degradation of DNA,

an all-in-one natural intumescent flame retardant

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Abstract

Very recently, deoxyribonucleic acid (DNA) has proven to be an efficient renewable, natural flame suppressant and retardant, due to its intrinsic intumescent features. In our previous work we have explored its flame retardant activity by applying as a surface coating on cotton fabrics and observed that on exposure to heat, the DNA was able to form a foamed char on the surface of the fabric. These remarkable results have stimulated this study on in-depth understanding of mechanism of thermal degradation of DNA. A number of characterization techniques have been exploited to investigate DNA decomposition, namely: thermogravimetry coupled to infrared spectroscopy or combined with differential thermal analysis, pyrolysis-combustion flow calorimetry and analysis of degradation residues. A scheme of DNA degradation mechanism is proposed to account for the results of the study.

Keywords: Thermal degradation; TGA; TGA-IR; Pyrolysis-Combustion Flow Calorimeter; Intumescent flame retardants

1. Introduction

The fundamental aspects about DNA and its role in the human, animal or vegetal life are widely known [1]. More specifically, DNA is responsible for the storage of biological information; a gene is a segment of the DNA molecule that contains all the information necessary for the synthesis of functional biological products. DNA operation is related to its complex chemical structure, in which each component plays a specific role. In detail, DNA is a polyelectrolyte in which the monomeric unit is a nucleotide having three characteristic components: organic nitrogenous bases (adenine (-A-), guanine (-G-), cytosine (-C-) and thymine (-T-)), a pentose unit (deoxyribose), and a phosphate group. The nucleotides are covalently bonded making a linear macromolecular structure through phosphodiester linkages. By this way, DNA backbone consists of alternating phosphate and pentose residues, while the nitrogenous bases are side groups connected to the skeleton at regular intervals. In addition, hydrogen bonds formed between the bases allow a complementary supramolecular association of two strands of nucleic acids, thus giving rise to the well-known double helix structure. An example of such interactions between cytosine and guanine is reported in Scheme 1, where in addition the repetitive unit consisting of glycosidic ring and phosphate groups are distinguishable.

DNA has been found to provide flame retardant properties to cotton [2-4] or to poly(ethylene-co-vinylacetate), EVA [5]. The three constituents of DNA can be related to a proper intumescent flame retardant formulation since an intumescent material typically consists of three chemical components [6-11]: i) an acid source acting as a char promoter (e.g. ammonium phosphates or polyphosphates), ii) a char source (e.g. pentaerythritol, arabitol, sorbitol, inositol, saccharides, polysaccharides, etc.), and iii) a blowing agent (e.g. urea, guanidine, melamine, etc.), which, upon heating, releases great amounts of gases (e.g. ammonia and/or carbon dioxide). When an intumescent material is subjected to a heat flow, it develops a multicellular foamed carbonaceous shield on its surface, commonly called *char*. This protection acts as a physical barrier able to limit the heat, fuel and oxygen transfer

between flame and polymer, leading to flame extinguishment. The same mechanism has been assessed by us for DNA when applied as a flame retardant to cotton fabrics or EVA [2-5].

DNA is commercially available. One source currently available (ca. 1000 T/year) use DNA derived from fishing industry waste, e.g. discarded salmon milt and roe sacs. It is used in electronics and cosmetics industries [12]. Despite the relatively higher current price of DNA with respect to other traditional flame retardants (FRs), this environmentally friendly, renewable, natural macromolecule is becoming quite interesting in fire science and technology. If it is proved to be commercially viable as a flame retardant for biomaterials, it can promote exploration of DNA production from cheaper sources and processes such as from biomasses wastes. This study addresses the thermal degradation of DNA, simulating its exposure to a heating source.

2. Experimental Part

2.1 Materials

DNA from herring sperm and cytosine powders were purchased from Sigma-Aldrich S.r.l. (Milano, Italy) and stored at 4°C before use.

2.2 *Characterization techniques*

Thermogravimetry (TGA) or High Resolution TGA (HRTGA) (Q500 TA Instrument thermobalance) and simultaneous TGA-Differential Thermal Analysis (TGA/DTA, SDT 2960 TA Instruments equipment) analyses were carried out on 10mg samples heated in Pt pans either in nitrogen or air (100ml/min) from 50 to 800°C at 10°C/min. In particular, TGA and TGA/DTA were employed to investigate DNA's thermal stability at standard heating rates (namely, 10°C/min); on the other hand, HRTGA was employed as a useful tool to thoroughly study very small weight losses (<5wt.-%) that were not completely distinguishable by TGA; indeed, in such conditions, HRTGA automatically reduced the heating rate from 10 to 1°C/min. Evolved gas analysis was performed on standard TGA (heating rate=10°C/min) coupled with infrared spectroscopy (TGA-IR, Nicolet iS10,

Thermo-Scientific). Isothermal runs were carried out for 3min by using Q500 TA equipment, sequentially heating the sample at 10°C/min in air to the temperatures corresponding to each weight loss step, as detected by TGA.

Thermal degradation residues were analysed by FTIR spectroscopy. The spectra were recorded at room temperature in the range 650-4000cm^{-1} (64 scans and 4cm^{-1} resolution), using a Thermo Avatar 370 spectrophotometer, equipped with attenuated total reflection accessory (ATR) and a diamond crystal. The association between the chemical structure evolution of the residues obtained from heating DNA in air, as assessed from their infrared, and the volatile chemicals simultaneously produced, was based on infrared spectra of the gases evolved in TGA-IR carried out in air, at temperatures corresponding to those of residues generation.

The data obtained from standard thermogravimetry (heating rate=10°C/min), in the range 20-700°C were compared with those of a Pyrolysis-Combustion Flow Calorimeter (PCFC, FAA Micro Calorimeter, Fire Testing Technology), in which pyrolysis was carried out at 60°C/min. Owing to the different heating rate and instrument heating geometry, volatiles evolution and corresponding heat release from their combustion were detected with a temperature shift by thermogravimetry and PCFC.

The morphology of DNA residues from isothermal TGA tests was investigated by using a LEO-1450VP Scanning Electron Microscope (beam voltages: 20kV). To this aim, DNA powder was deposited onto conductive adhesive tapes and then gold-metallized.

3. Results

3.1 Overall DNA thermal behaviour

In Figure 1A, DNA TGs in air and nitrogen are reported: they show similar weight loss curves in both atmospheres, apart from a slightly larger weight loss mostly between 250-350°C in nitrogen than in air, which shows a general low oxygen sensitivity of DNA in thermal degradation conditions. Thermal decomposition occurs through a number of steps following the removal of

absorbed water, which is completed at 100-150°C, depending on heating rate and corresponding to about 8% weight loss.

Three temperature ranges can be conveniently considered to describe the DNA weight loss during heating: the first, from 150 to 200°C, corresponds to a low weight loss (<10%), while the second and third between 200-400 and 400-700°C respectively, involve about 20% weight loss each (Figure 1B).

In the first range, below 200°C, two sharp weight losses are detected by HRTGA to occur at relatively high rate with maxima at 160 and 187°C respectively (Figures 1C, 1D and Figure 2A). On heating at 10°C/min, the two steps merge in a single weight loss, with a four time slower process, as can be seen from scales of the graphs, with maximum rate at 180°C (Figure 1B) and exothermal heat balance (Figure 2B) with production of a small amount of combustible volatiles, as assessed by PCFC (Figure 2C). Although the corresponding weight losses (1 and 5wt.-%, respectively) are almost negligible, DNA undergoes a significant physical modification in this stage as shown in Figure 3. The grains of the original white powder (Figure 3A) are blown to hard, blackish/red spherical particles (diameter 300μm, Figure 3B), the internal structure of which is made of closed spherical cells as shown by the cross-section in Figure 3C. This is the typical behaviour of intumescent fire retardant materials, which decompose on heating forming a thermally stable blown foamed structure [6-11].

In 200 and 400°C temperature range, a 20% weight loss occurs in two partially overlapping processes (Figure 1). The first process takes place with maximum weight loss rate at 230°C in TGA either in air or nitrogen or in HRTG in air, thus resulting independent from atmosphere and heating rate. In this weight loss step, the close cells structure assumed by DNA degraded to 200°C is disrupted with the formation of an open cells structure as if gases trapped and/or evolved in the closed cells of Figure 3B blew them up on heating (Figure 3D).

The second process occurs with maximum rate at 267°C in TGA and HRTGA, respectively, under nitrogen and air, or at 350°C in TGA in air.

It is in this temperature range (200-400°C) that DNA decomposition is combined with the production of the largest fraction of volatile combustible products, as shown by PCFC (Figure 2C). The resulting residue, on further heating, looses 20% weight at a constant slow rate between 400-700°C (Figure 1A), indicating that it becomes more and more stable through a progressive chemical restructuration promoted by heating. At 700°C the residue amounts at 48%. On low heating rate in HRTGA in air, the DNA residue obtained at 400°C follows the behaviour found at 10°C/min heating until 600°C, when it undergoes a sharp weight loss with maximum rate at 630°C, leaving a 28% residue stable to 700°C.

The DNA thermal behaviour indicates that, on heating, it produces a large yield (28 to 48%) of a solid residue characterised by outstanding thermal and thermal oxidative resistance, typical of inorganic/ceramic materials. Indeed, literature shows that all carbon-rich residues obtained from organic compounds thermal degradation (e.g. cellulosic chars), thermally oxidise to volatiles (burn) around 500-650°C in TGA in air, depending on their chemical structure on their aromatisation level, as already demonstrated [13, 14]. Indeed, evidence of partial occurrence of this process in air is also seen in Figure 1B by the broad small weight loss rate peak at about 520°C, as shown by TGA and by a similar more relevant weight loss at 630°C in HRTGA (Figure 1D).

This finding suggests that the DNA thermal stabilisation that occurs in both nitrogen and air is due to the heat promotion of either cyclisation or crosslinking or aromatisation processes, which confer thermal and oxidative resistance to organic molecules without significant degradation to volatiles formation. The very high thermal stability at T> 700°C is then likely to be the result of slow transformation of the residue in a ceramic-like material, possibly P-N rich, as in the case of melamine phosphate thermal degradation [15].

3.2 DNA chemical evolution on thermal degradation

The complex process of DNA thermal degradation involves a progressive transformation of its chemical structure throughout the weight loss temperature range, as shown by the infrared spectra

of the residues produced by DNA isothermal heating at selected temperatures in the range 180-600°C (Figure 4). By the related residual weight reported in Table1, the chemical structure of the degrading DNA (Figure 4) can be associated to the weight loss steps shown by the curves of Figure 1.

Table 1. DNA residue left after isothermal tests by TGA.

Temperature [°C]	Residual weight [%]
180	90
230	83
300	73
350	64
400	58
450	58
500	53
600	49
700	47

The DNA chemical building blocks show up in four regions of its IR absorption spectrum (Figure 4): in the 1800–1500cm^{-1} region, absorptions are due to vibration of the bases bonds; in the 1500–1300cm^{-1} region, to vibrational coupling between the base–sugar entities reflecting glycosidic bond rotation; in the 1300–1100cm^{-1} region, to vibrations along the sugar–phosphate chain; in the 1100–800 cm^{-1} region, to sugar/sugar–phosphate vibrations [16]. Figure 4 shows that progressive substantial changes occur in all the various DNA building blocks with increasing the DNA temperature treatment.

In the following, infrared of residues of the relevant steps observed in the thermal analysis of Figure 1 (TGA), are combined with the chemical nature of produced volatiles identified in TGA-FTIR (under dynamic conditions), aiming to understand the chemical processes occurring on DNA heating.

3.2.1. 50-180°C

The DNA chemical modifications involved in this degradation step concerning the intumescent behavior are shown by the ATR spectra of Figure 5. A broad band centered at 3000cm^{-1} appears, as well as a strong absorption at 890cm^{-1} that is in the region of finger print vibrations and a small absorption growth at 1430-1475cm^{-1}. The infrared spectrum of volatiles evolved besides the presence of water and CO_2, shows an absorption (2380cm^{-1}) due to isocyanic acid (Figure 6A) [17], which may be the combustible volatile producing the small exothermal effect in the PCFC (Figure 2C).

3.2.2. 180-230°C

On increasing the temperature to 230°C, the DNA residue closed cells disruption occurs likely to be due to pressure increase of gases trapped in the cells, which produces the open cells structure of Figure 3D. Indeed, up to 200°C, volatiles evolved detected by infrared are those of Figure 6A. However, at 230°C, ammonia is detected (doublet at 960-930cm^{-1}) among volatiles besides water and CO_2, whereas isocyanic acid is no longer present (Figure 6B). The infrared spectrum of the residue at 230°C, as compared to that at 180°C shows a further increase of the absorptions at 1425cm^{-1} and disappearance of the absorption at 950 cm^{-1} (Figure 7A).

3.2.3. 230-400°C

From 230 to 400°C the residue becomes completely black and the ATR spectra at 350°C (Figure 7B) show that the band at 1662cm^{-1} is replaced by an absorption at 1580cm^{-1}, which shows as a shoulder at 300°C. Additional absorptions at 980 and 756cm^{-1} grow besides the absorption at 885cm^{-1} developed on heating DNA to 180°C, giving rise to the typical triplet in the range 700-900cm^{-1}attributed to CH wagging of aromatic structures [18].

As far as the volatile species detected by TGA-IR in this temperature range are concerned, the same gases observed at lower temperatures (H_2O, CO_2 and NH_3) are seen, among which again ammonia is the combustible volatile (Figure 2C).

3.2.4. 400-700°C

In the range between 400 and 700°C (Figure 8), CO and CO_2 are the gases evolved, while the infrared spectra of the residues show a decrease of the aromatic absorptions at 756 and 980cm^{-1}, above 450°C. Indeed, at 350°C DNA has still a residue of 68% that is reduced to 56% at 520°C and subsequently to 40% at 700°C (Figure 1A).

4. Discussion

The DNA's intumescent-type thermal behaviour is related to its fire retardant activity. Intumescence of DNA occurs at a relatively low temperature, 170-200°C as compared to intumescent model compound such as pentaerhytritol diphosphate (PEDP), which activates at 300-350°C [9, 10, 19, 20]. As in the case of PEDP, a relatively low weight loss takes place (7% as compared to 20% in PEDP), while the white powder material is blown into hard blackish-red multicellular foamed spherical particles (Figure 3). Water, CO_2 and isocyanic acid are simultaneously evolved while OH groups appear in the residue, in which there is also indication of finger print structure modifications (<1100cm^{-1}).

This behaviour involves transition of DNA from a solid to a viscous liquid on heating, with simultaneous thermal decomposition of weak chemical structures that produce the blowing gases. The thermally induced bonds scission is however limited, leading to a stable macromolecular structure, which is essential to the viscoelasticity required by the blowing action.

DNA intumescent behaviour confirms that the blowing action can be performed by a very limited weight of volatiles (7%, Figure 1) since a mole of "ideal" gas occupies 22 litres at room pressure and temperature. Thus, assuming that in this step, water and CO_2 were produced in equal amount,

an average 31 molecular weight would result for the volatiles evolved and the volume corresponding to 7% by weight evolved by 1g of DNA would then be that occupied by 0.03 mole of gas that is 0.5 litres measured at 200°C and 1atm.

The single bonds due to sugar-bases C-N (293kJ/mol) and sugar-phosphate PO-C (358kJ/mol) exocyclic are the thermally weakest bonds in DNA structure (Scheme 1). This suggests that at relatively low heating rate (as in Figure 1A), sugar-base bonds should mainly break in the first degradation step between 160-200°C as shown in Scheme 1 for the DNA section involving cytosine-guanine hydrogen bonded complex. On the other hand, it has been shown that triethylphosphate, which contains phosphate ester bonds that could be a sort of model molecule for DNA, undergoes pyrolysis at around 230°C [21].

Splitting of the bases leaves behind unsaturated sugar-phosphate chains and leads to condensation of the bases into a structure that is thermally stable at the C-N splitting temperature. Indeed, the DNA bases can give condensation reactions on heating, as shown for example in Figure 9 for the purine base cytosine, which on heating produces about 60% of a material ("char") thermally stable in nitrogen at least up to 800°C and oxidising in air at 500°C.

The condensation process is likely to occur through classic alkylimino-de-oxo-bi-substitution that is the nucleophilic addition of the cytosine primary amine group onto the carbonyl group. In DNA, the condensation would occur between carbonyls and primary or secondary amino groups of purine and pyrimidine bases, as shown by examples in Scheme 2, respectively for cytosine-guanine condensation. The hydrogen bonding between the DNA bases, holding together the two strands of the double helix supramolecular assembly structure, exceeds the typical low thermal stability of hydrogen bonding owing to its cooperative nature. Therefore, at the temperature of C-N sugar-bases bonds breaking, the carbonyl-amine hydrogen bonded complexes would still be stable and thus lower the condensation energy of activation as compared for example to the case of cytosine shown in Figure 11: as a consequence, condensation occurs at a lower temperature than in cytosine.

Scheme 2 concerning the addition of primary amine gives a hemiaminal (I), which is unstable and eliminates water leading to primary ketimine bonds (II), in agreement with the water evolution detected on heating DNA (Figure 6A). The secondary amine addition (Scheme 2 route B) gives a hemiaminal (IV), which may further react with an amine group eliminating water to give an aminal (not shown here) or could give an enamine by water elimination involving the α-carbonyl proton (V).

Since the DNA bases contain two (adenine) or three (cytosine, guanine, thymine) functions available for the alkylimino-de-oxo-bisubstitution, the condensation process can proceed to build a crosslinked macromolecular structure as in a typical multifunctional polycondensation polymerisation. Polymerisation may also occur through a regular polyaddition as in Scheme 2 to form a polyimine (III) or tautomer (III') or (VI), respectively, which would crosslink for example by condensation of primary and/or secondary amino groups with carbonyl groups.

An approximate thermal balance calculation of the ketoimine formation, based on bonds energy, including water evaporation, gives an exothermal balance of about 250kJ/mol, thus qualitatively accounting for the exothermal behaviour shown in DTA reported in Figure 2B, concerning the range of temperature, in which intumescence occurs. An exothermal intumescent process was similarly revealed in the case of PEDP model compound and is the result of condensation-cyclisation reactions following the initial bond breaking, which produces the thermally stable blown residue most often called "char" even if it contains little or no carbon [9, 10, 19, 20].

The infrared spectrum of the intumescent material produced by DNA thermally induced reactions shows build-up of OH absorption at 3000cm^{-1} (Figure 5). This is due to OH groups of hemiaminals, which could not eliminate water owing to absence of α-carbonyl proton as for example in the case of amine addition to the carbonyl group of (V). The other most noticeable modification of the infrared spectrum is the increase of an absorption at 890 cm^{-1}in the finger print region, which is in agreement with the DNA structure modification of Figure 9. The DNA bases condensation reactions lead to conversion of carbonyl groups into C=N bonds that are not detectable in the 180°C residue

infrared because they are already present in the DNA bases adenine, cytosine and guanine. However, conversion of CO to C=N is in agreement with shift of the DNA absorption from 1680 to 1650cm^{-1}.

Among the gases evolved during the intumescence step, CO_2 and HNCO are detected besides water (Figure 6A, the formation of which can be explained by hydrolysis of the thymine base cycloimide structure by the water produced in condensation reactions of Scheme 3, followed by thermal degradation of the resulting linear compound. An unsaturated amine is also formed in such reaction, which may undergo the carbonyl condensation reaction with the DNA bases.

Above 200°C, the weight loss becomes more relevant, CO_2 being the major volatile produced besides water and ammonia. The infrared spectrum of the residue left at 230°C shows an important increase of the broad, hydrogen bonded OH absorption at 3000cm^{-1}, a shift of the DNA absorption in the region of sugar-phosphate chain at 1260 to 1210cm^{-1} (Figure 7A) and the absorption at 875-885 cm^{-1} becomes the dominant absorption in the finger print region.

These experimental findings point to phosphoester pyrolysis of the 2,3 dihydrofuran 3,5 phosphate diester polymer (VII) producing the 2,3 dihydrofuran 3 phosphate 5 exo-methylene (VIII), which could then condense with water elimination to produce the pyrophosphate (IX) or to polymerise (X) in agreement with water found as a volatile product (Scheme 4). Accordingly, a progressive modification of the infrared spectrum of the residues is observed in Figures 7B and 8 involving the four regions typical of the original DNA structural building blocks [1], leading at 700°C to a spectrum characterised by absorptions at 1280, 900 and 730cm^{-1} that cannot be associated to an organic structure but rather to an inorganic material. This is in agreement with the thermal resistance of DNA residue of thermal degradation reaching at least 700°C.

The kind of self-curing process taking place above 400°C is likely to involve crosslinking reactions between the phosphorous and nitrogen based condensates described in Schemes 1,2 and 4, involving acidic phosphorous and basic nitrogen groups that create thermally stable P-N based structures. Carbon may be trapped and thermally stabilised in such structures. These processes

involving a competition between volatilisation and structure strengthening, should be kinetically controlled. Indeed, it is seen in Figure 1 that in HRTGA, oxygen has time to react with the condensate material in a sharp weight loss step at 600°C, before its conversion into the inorganic material stable at 700°C. This corresponds to the thermal oxidative volatilisation of the typical base condensate obtained on heating cytosine in Figure 9.

5. CONCLUSIONS

DNA is shown to decompose on heating, producing an intumescent effect that is it undergoes a transformation into a multicellular, foamed, thermally insulating material at a relatively low temperature (160-200°C) as compared to typical intumescent fire retardant additives (e.g. 300-350°C) reported in literature. This may be the reason for the DNA high fire retardant effectiveness particularly when DNA is layered onto polymer surface. The intumescent fire protection screen is thus formed at a lower temperature than that at which thermal decomposition of organic polymers occurs.

Furthermore, the chemical composition of the intumescent residue on heat exposure is converted into a highly thermally stable ceramic-like material which is resistant to thermal oxidation unlike organically derived intumescent chars and hence, preserves the intumescent fire barrier properties. Thus, the fire protection built by DNA decomposition can withstand fire exposure for longer time than traditional intumescent fire retardants.

The peculiar behaviour of DNA fire protection action derives not only from the presence of the classical three ingredients of intumescent formulations in its structure, i.e., hat is char source and catalyst and foaming agent but also from its supramolecular assembled structure in which the three components are molecularly organised.

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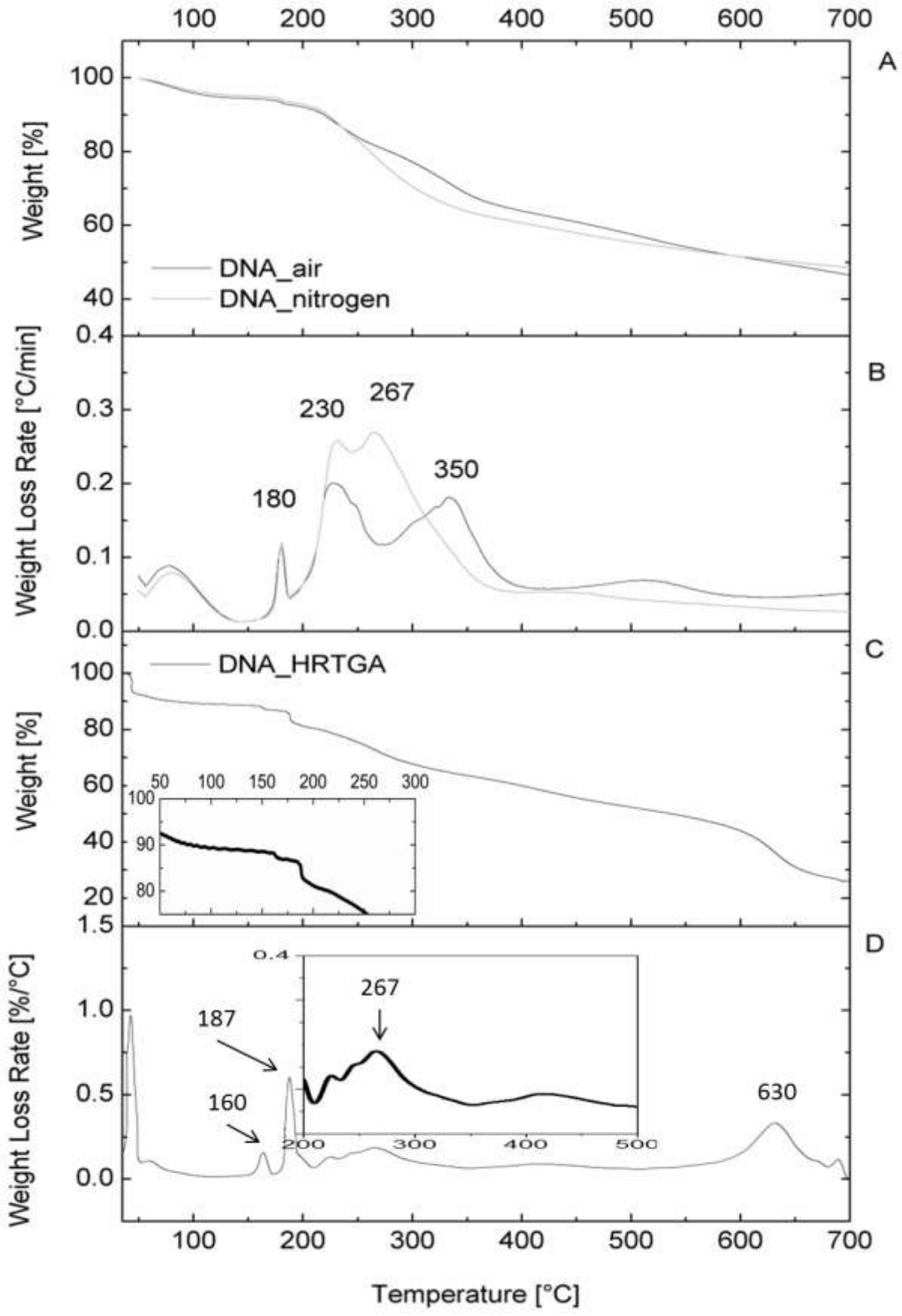

Figure 1. TG, DTG, HRTG and dHRTG curves of DNA.

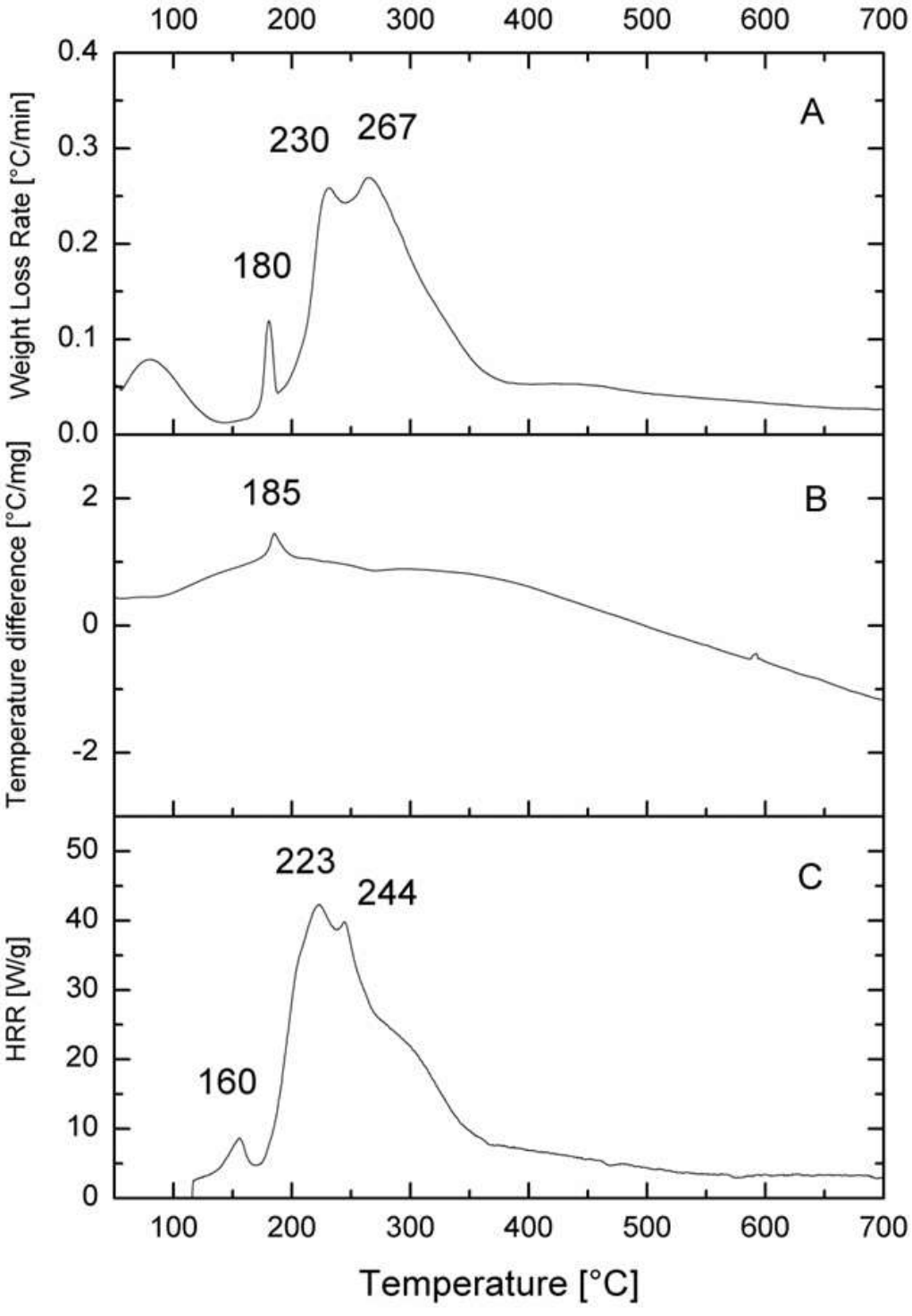

Figure 2. TG, DTA and HRR curves of DNA.

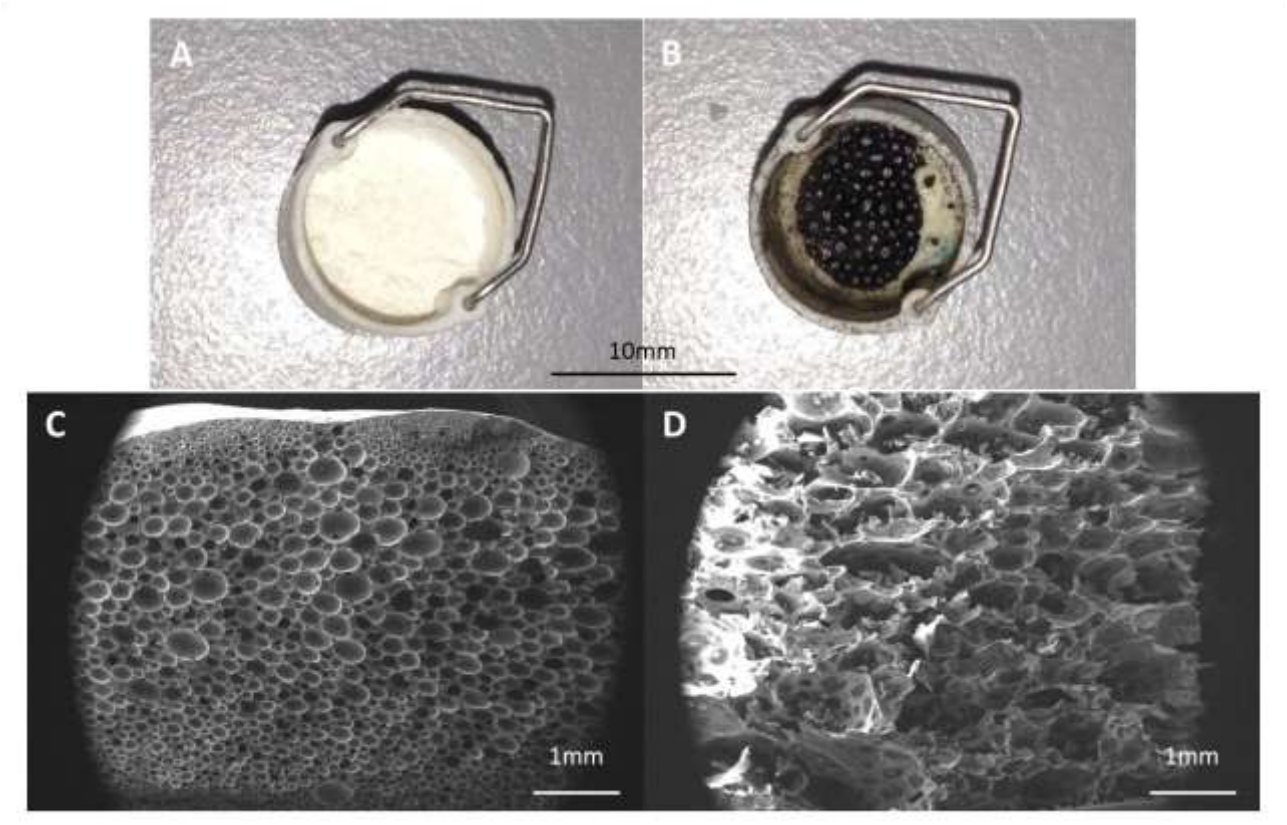

Figure 3. Picture of DNA powder (A), DNA residue at 180°C (B), SEM magnification of the DNA residue at 180 (C) and 230°C (D).

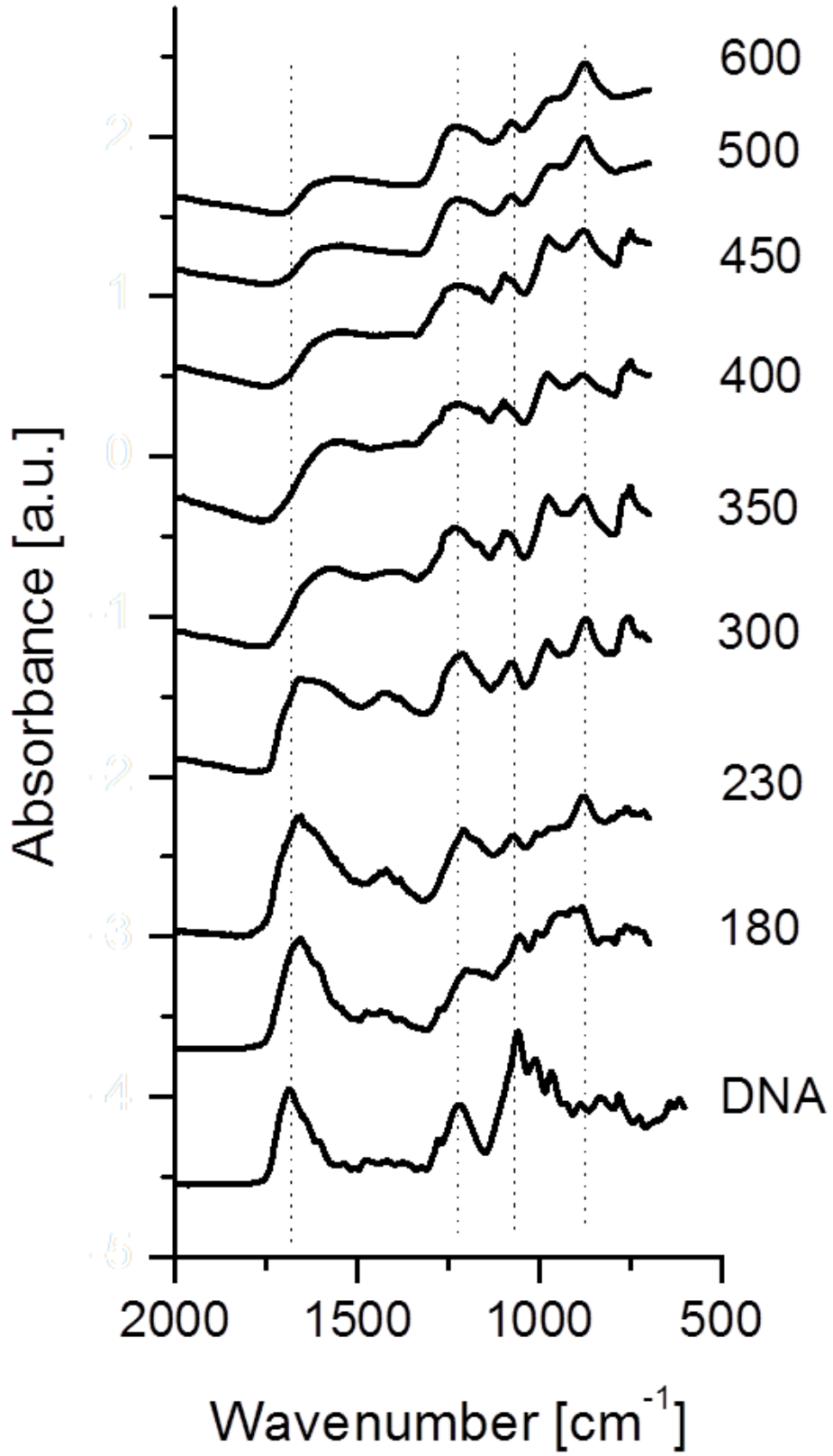

Figure 4. ATR-FTIR spectra of DNA and its residues from 180 to 700°C.

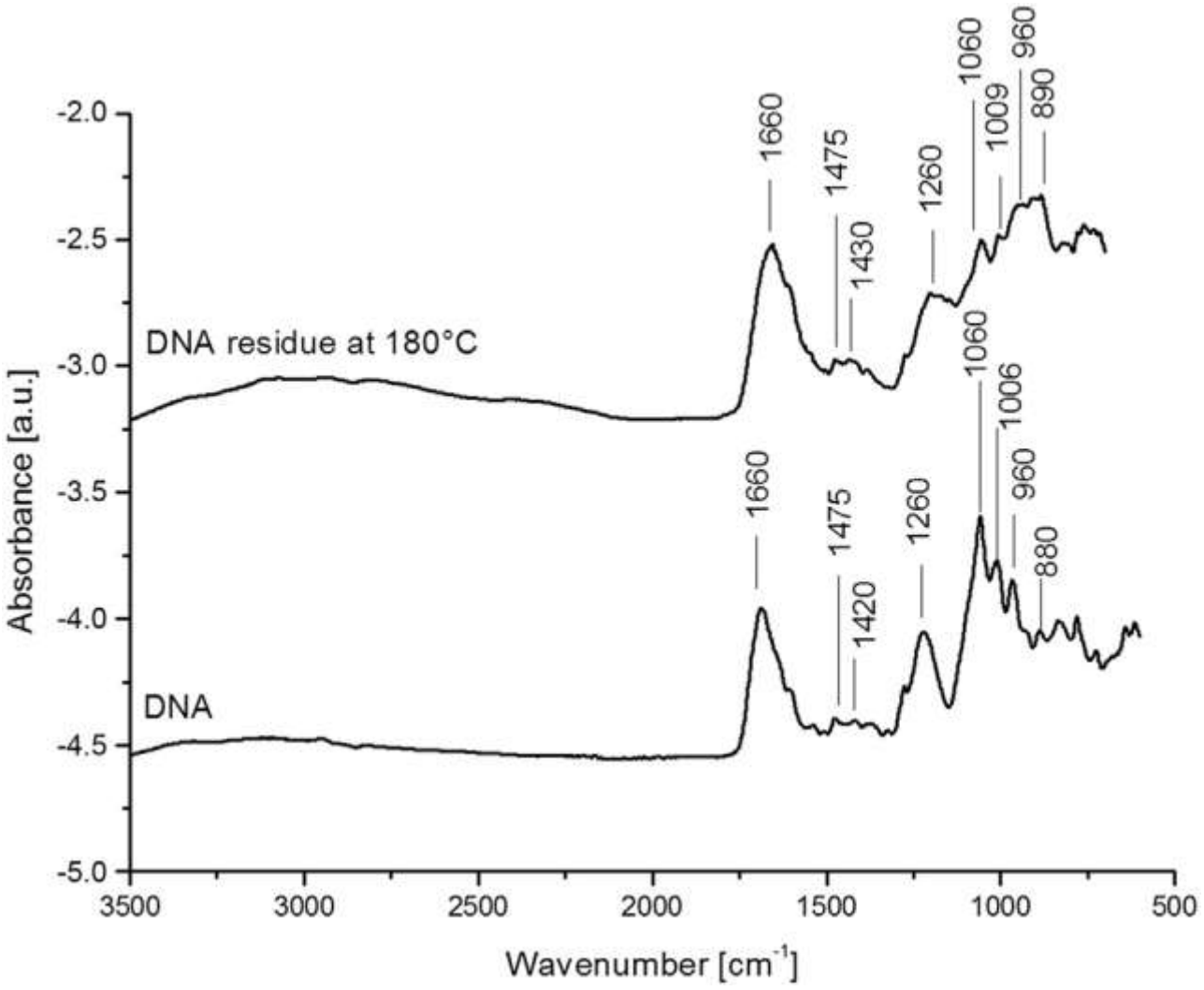

Figure 5. ATR-FTIR spectra of DNA and its residue at 180°C.

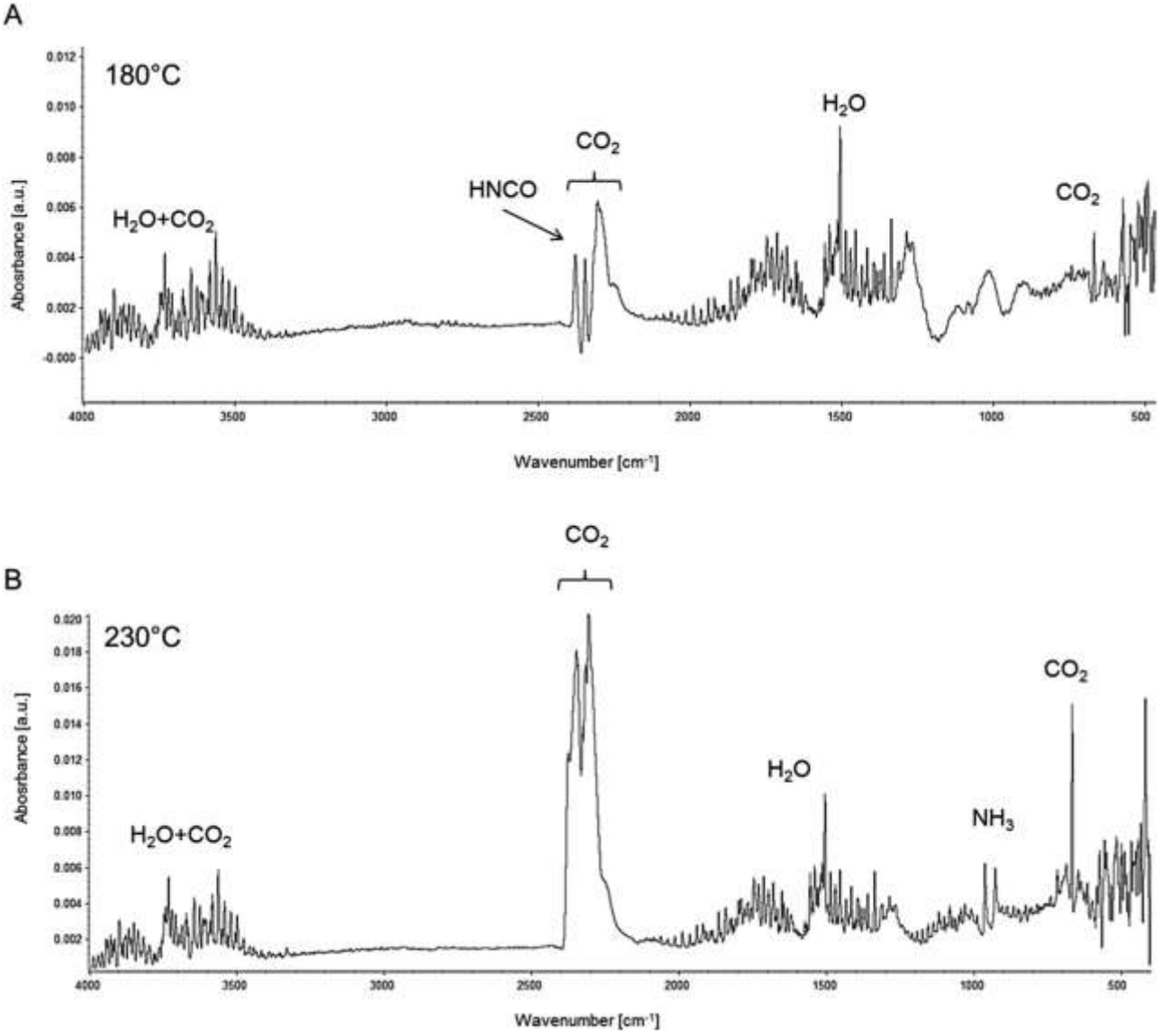

Figure 6. TGA-FTIR spectrum of DNA at 180°C (A) and 230°C (B) .

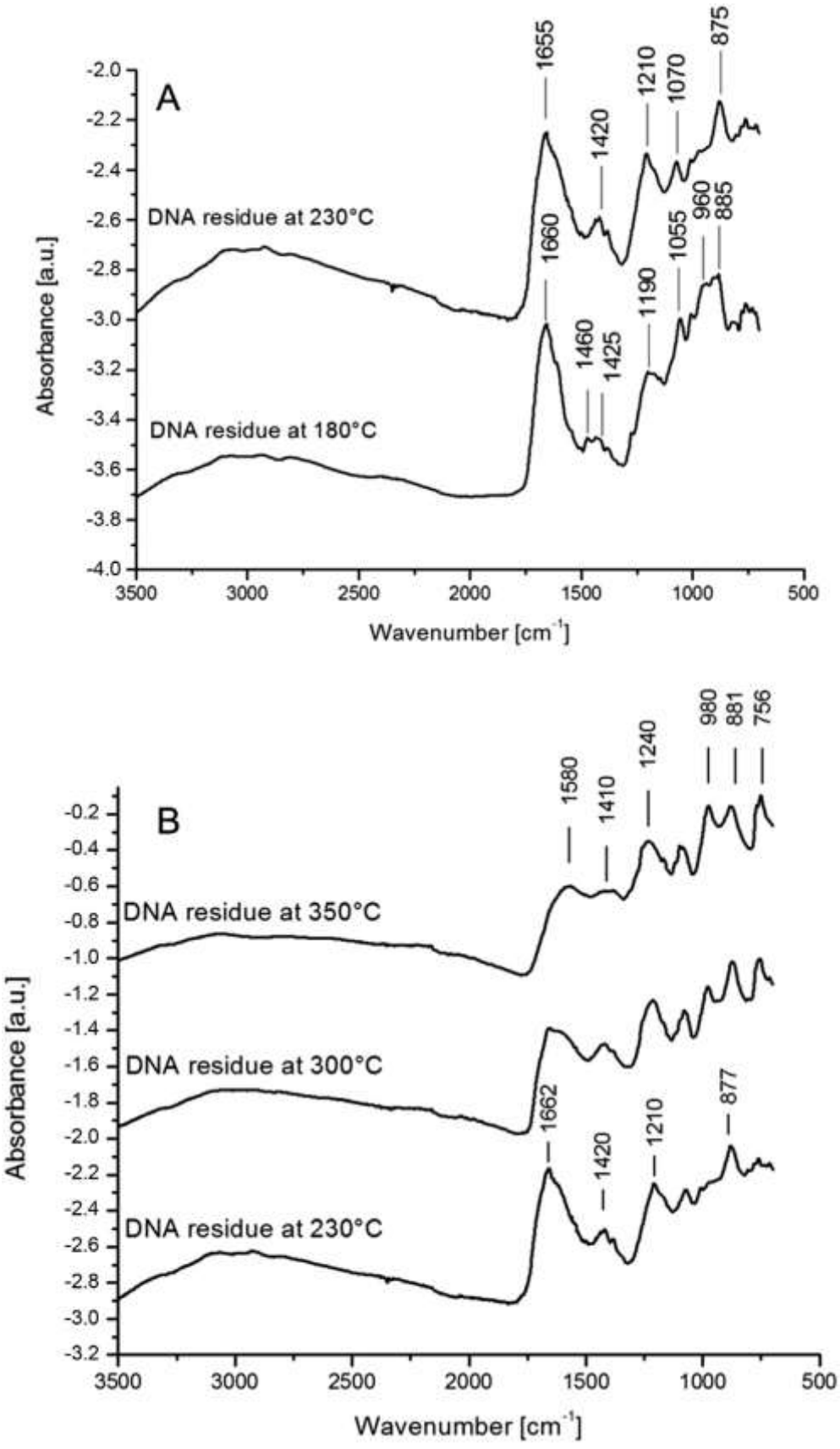

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Figure 7. ATR-FTIR spectra of the residues at 180 and 230°C (A) and at 230, 300 and 350°C (B).

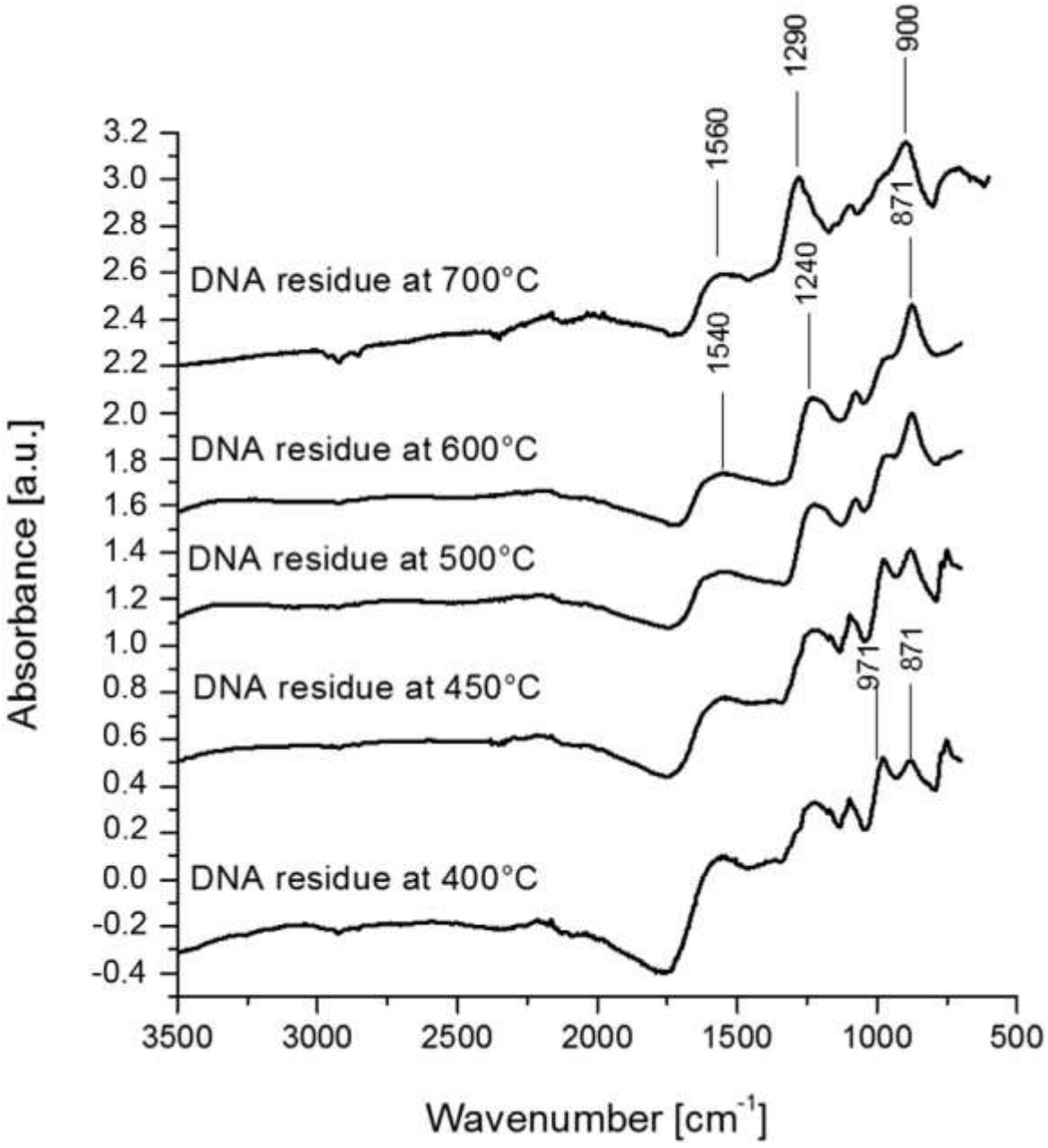


Figure 8. ATR-FTIR spectra of the residues at 400, 450, 500, 600 and 700°C.

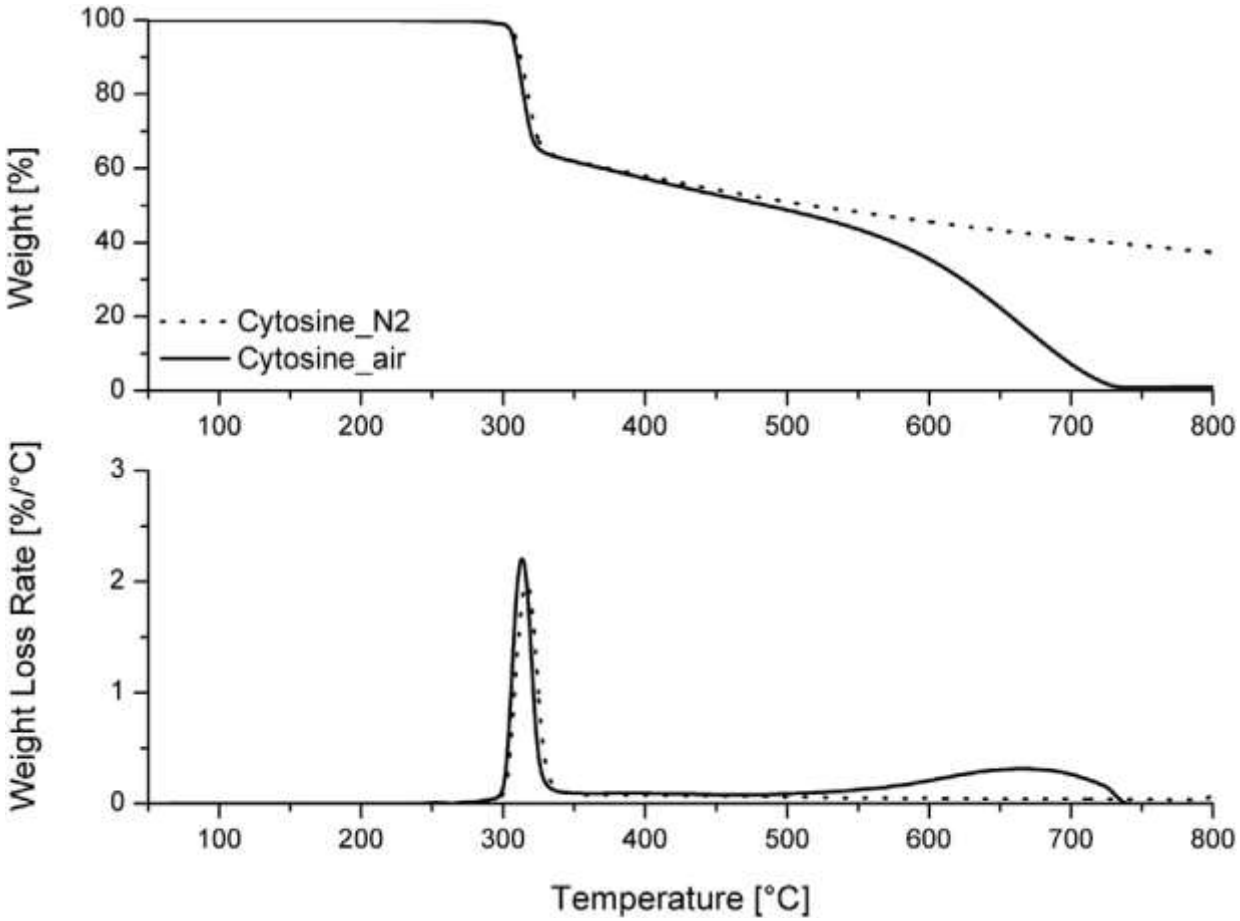
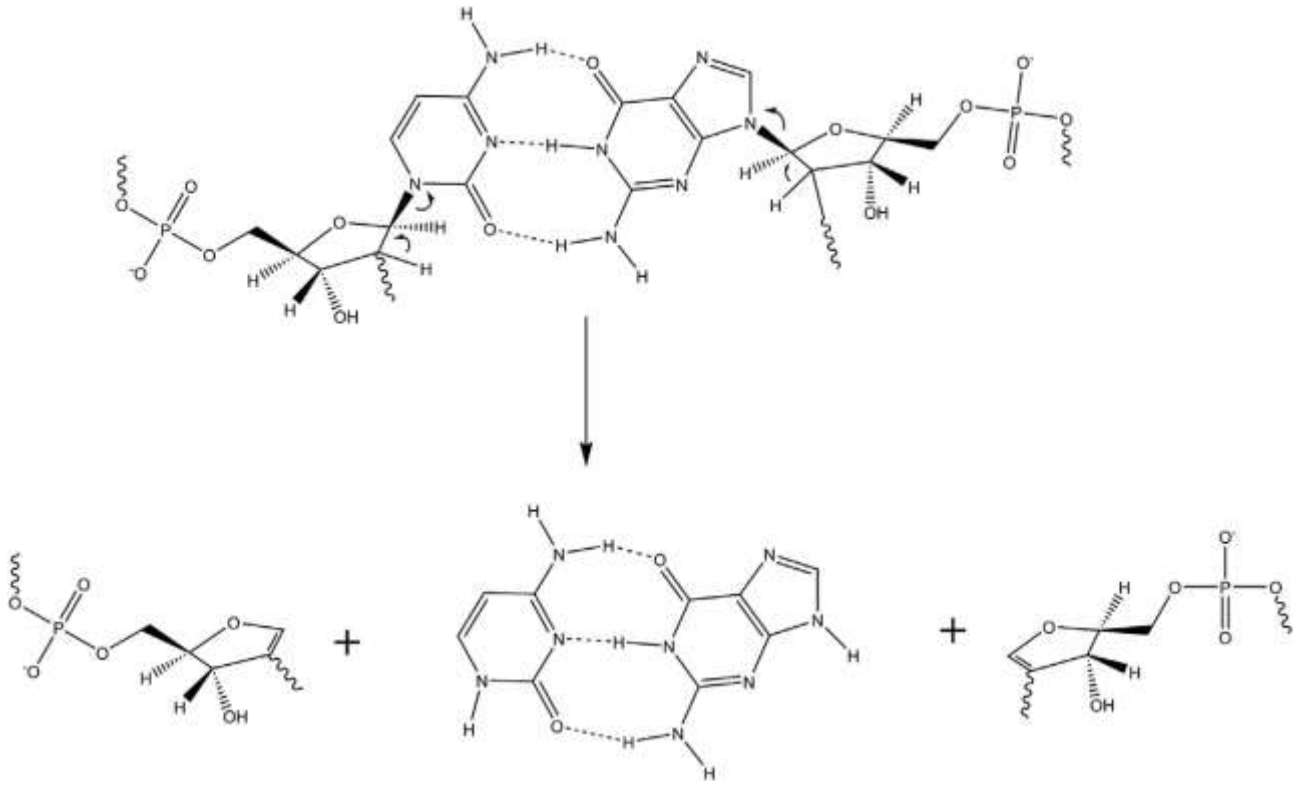
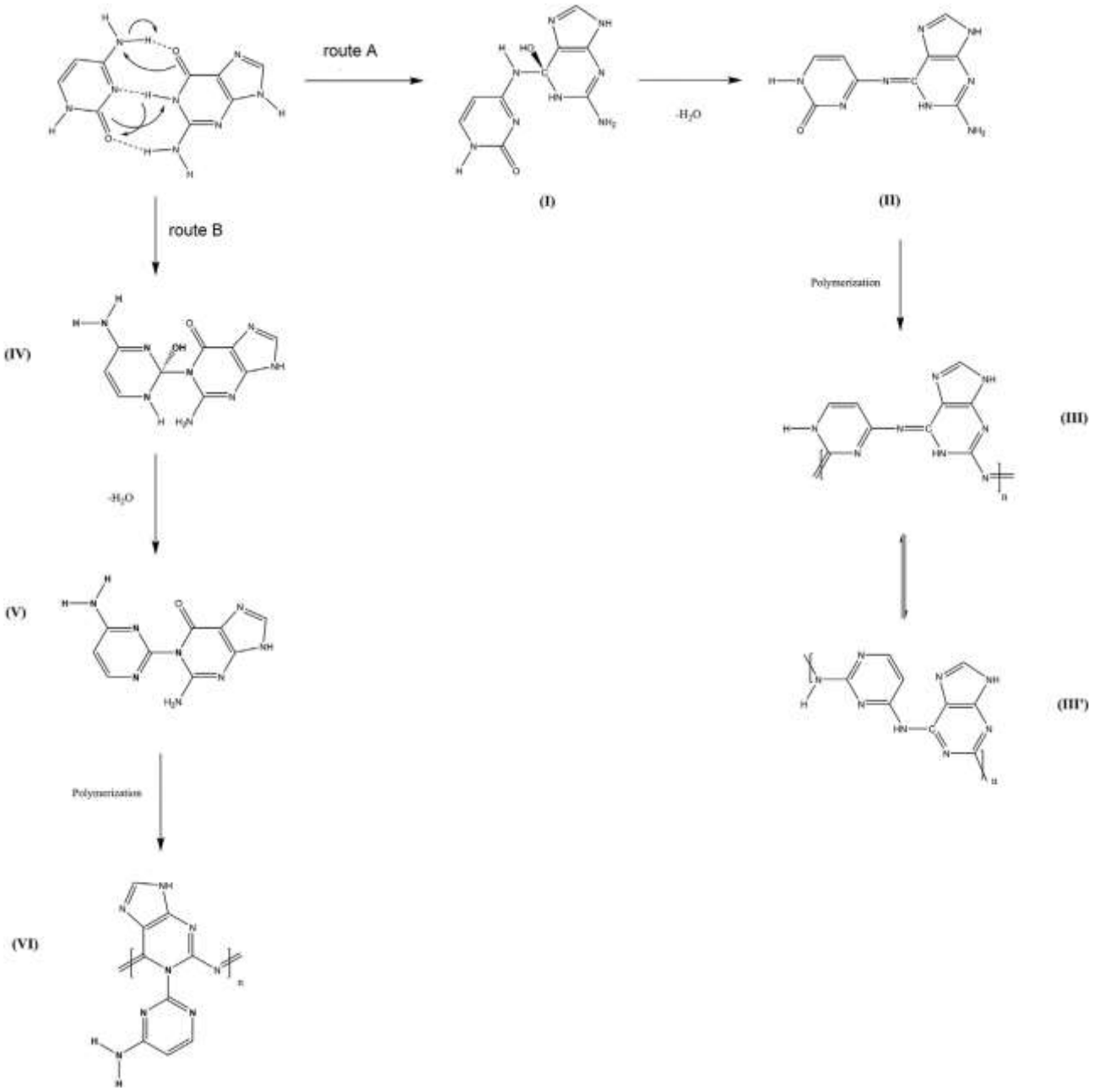


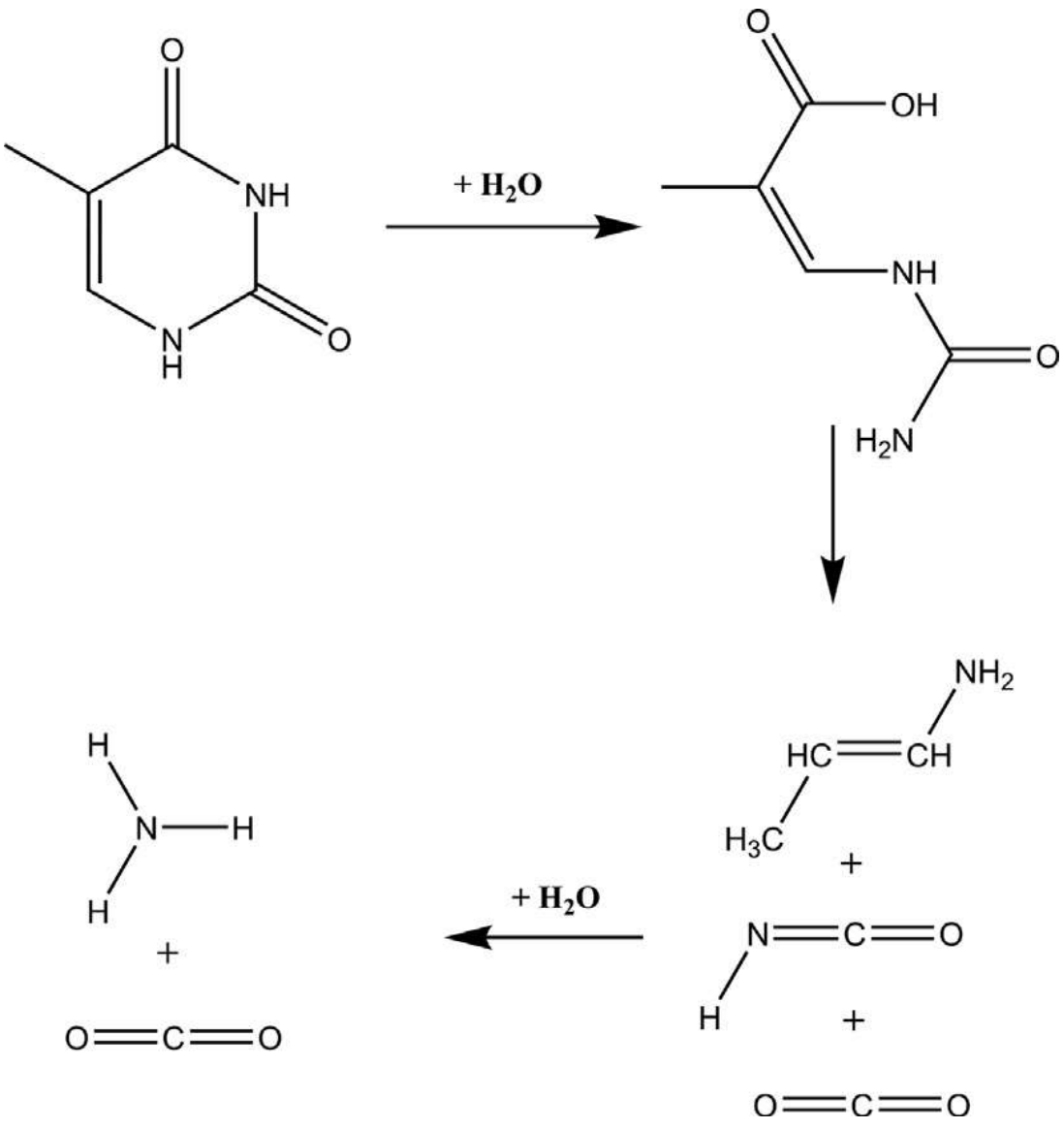
Figure 9. TG and dTG curves of cytosine in nitrogen and air.



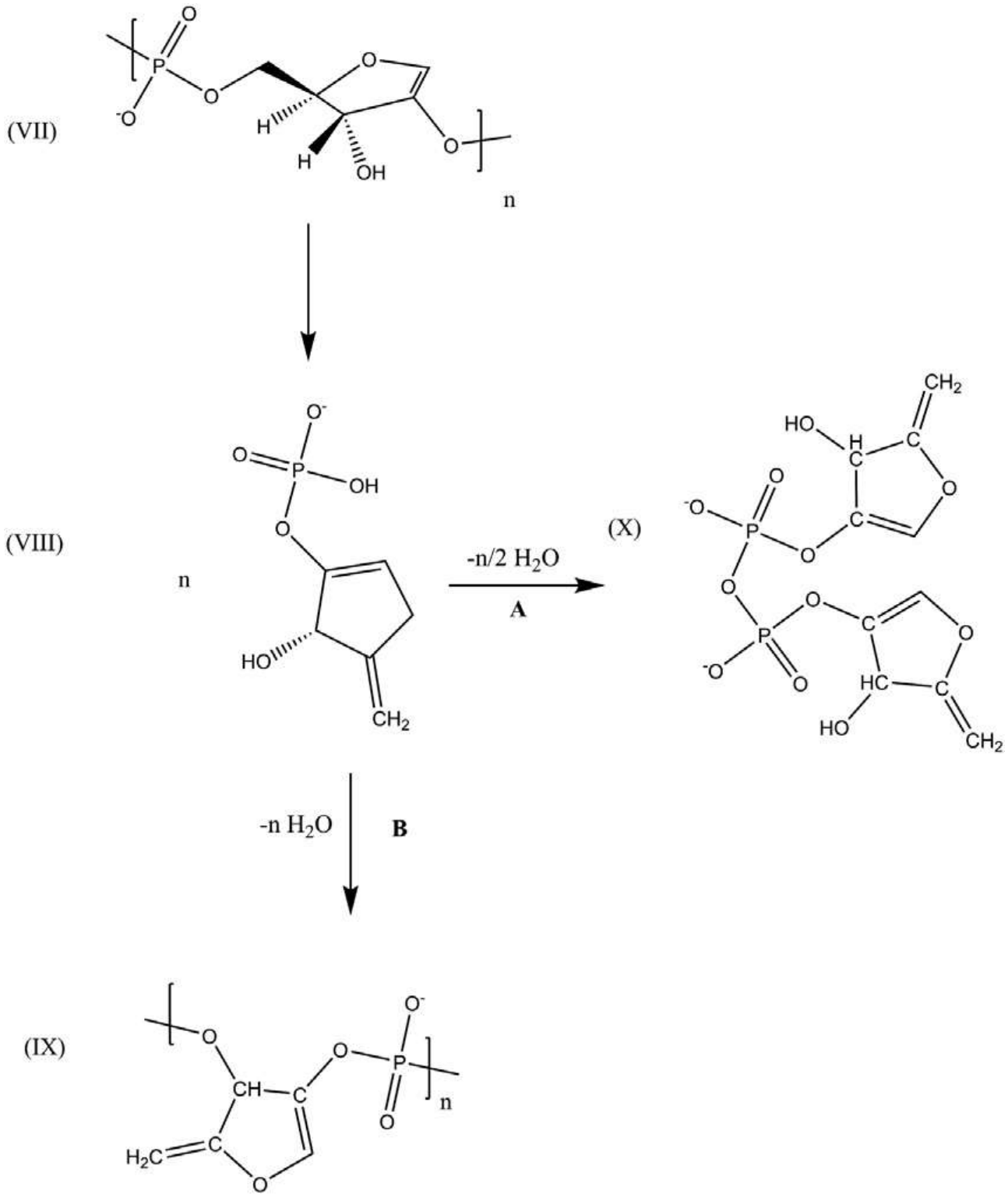
Scheme 1. Schematic representation of cytosine and guanine-based nucleotides and thermal scission of C-N and PO-C single bonds in sugar-bases and sugar-phosphate exocyclic, respectively.



Scheme 2. Reaction between primary amino group of cytosine (route A) and carbonyl group of guanine and secondary amino group of cytosine and carbonyl group of guanine (route B).



Scheme 4. Hydrolysis reaction of thymine.



Scheme 5. Pyrolysis of phosphoester containing fragments.